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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Coating and Joint-Sealing Compositions Contains
Alkylthio Substituted Aromatic Diamines as Hardeners for
Polyisocyanates

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COATING AND JOINT-SEALING COMPOSITIONS CONTAINS ALKYLTHIO
SUBSTITUTED AROMATIC DIAMINES AS HARDENERS FOR POLYISOCYANATES

ABSTRACT OF THE DISCLOSURE

The present invention relates to a coating composition or joint-sealing composition which may be cured at room temperature to form bubble-free products and contains

- i) a polyisocyanate component and
- ii) a hardener component containing
 - a) one or more aromatic diamines having at least one methyl substituent and at least one alkylthio substituent with 1 to 4 carbon atoms in the ortho position to each amino group and
 - b) optionally one or more organic polyhydroxyl compounds or organic polyamines other than those set forth in a).

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COATING AND JOINT-SEALING COMPOSITIONS CONTAINS ALKYLTHIO
SUBSTITUTED AROMATIC DIAMINES AS HARDENERS FOR POLYISOCYANATES

BACKGROUND OF THE INVENTION

Field of the Invention

5 The invention relates to two-component coating and joint-sealing compositions containing certain alkylthio-substituted aromatic diamines as hardeners for organic polyisocyanates.

Description of the Prior Art

10 Building structures made from mineral building materials, such as concrete, bricks, etc., are repeatedly exposed to a number of damaging effects which could seriously impair the period over which the building might remain sound. Included among these factors are the penetration of water, salt
15 solutions, liquid chemicals, acid components in the atmosphere, erosion of surfaces due to the effects of the weather or wear due to harsh mechanical wear and tear (exposure to friction or impact). In particular, penetration of moisture into building components contributes greatly to their wear by encouraging
20 degradation of the building material itself or the reinforcing steel, by impairing important properties such as the compressive strength and by enabling the growth of algae, lichens and fungi etc., as well as blooms of water-soluble salts, such as nitrates etc. Also, the living conditions inside the
25 buildings suffer considerably when moisture penetrates the building structure.

 Therefore, the surfaces of building structures are frequently protected with a waterproof, strongly adherent coating. The protective function of a coating is only
30 produced, however, if it has both an adequate elasticity (ability to stretch) and a certain minimum thickness.

There are numerous references to these interrelationships in the literature (for example in the article "Rißüberbrückende Beschichtungen für mineralische Baustoffe" (Coatings for bridging cracks in mineral building materials), G. Reiche, Farbe und Lack, 85 (1979), 824-831). In general it is required that a minimum thickness of 0.1 mm should be maintained. The coatings should be able to stretch at least 100%. In addition, the protective function of such coating materials is maintained for a particularly long time if the weather-resistance is relatively high, and even longer if the long-term properties of the coating are only slightly affected by weathering and environmental factors.

When choosing coating materials it should be noted that the surfaces to be coated are generally porous and therefore often contain a certain amount of water. If this "domestic moisture" in enclosed spaces is about 3.5% by weight of water, then the water content is frequently much higher when applying coatings in the open air. This may lead to problems, in particular, the formation of blisters in polyurethane coatings due to the release of carbon dioxide gas.

The coating systems recommended in DE-OS 3,203,490, which are based on NCO prepolymers and diprimary, alkyl substituted, aromatic diamines, have been proven as coating materials for the substrates mentioned insofar as they permit the production of thick, highly elastic, crack-bridging coatings, even on fairly damp substrates, without the formation of troublesome bubbles. The systems do have the disadvantage, however, that they do not have sufficient pot life due to the high reactivity of the diamines which are used. This may produce problems when the materials are intended to be processed at high ambient temperatures (tropical or sub-tropical climatic areas), or if a particularly long "open time" (pot life) is desired for other reasons. Another disadvantage of the high reactivity towards polyisocyanates of the diamines used according to the prior printed publication is that the hardener component consists

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exclusively of the diamine and not mixtures of the diamine with organic polyhydroxyl compounds. This is because the difference in reactivity between the diamine and the polyhydroxyl compounds is too great to enable a homogeneous reaction.

5 Basically the same comments apply to the systems in DE-OS 3,148,838 and US-PS 4,716,210. These are quick-setting two-component polyurethane systems which can only be applied by pouring or spraying using multi-component metering and mixing equipment.

10 It was an object of the present invention to provide new, two-component binders which permit the production of coating and joint-sealing compositions which do not have the disadvantages associated with the systems of the prior art. It is an additional object to provide coating compositions which have a comparatively long "open time," but which also have a
15 sufficiently high reactivity, in combination with certain polyisocyanates and in the presence of catalysts, to be efficiently useful in a mechanized series production. It is a further object of the present invention to be able to use the
20 diamines in combination with comparatively inexpensive polyhydroxyl compounds as hardeners for organic polyisocyanates to lower the overall cost. It is also an object to be able to produce the binders by simply mixing the individual components and to maintain final products which possess the mechanical
25 properties of the prior art systems.

Joint sealants ("joint-sealing compositions") are also frequently used in areas in which the residual moisture content exceeds the "domestic moisture" content of 3.5% by weight which is just tolerable by polyurethane materials. Accordingly, a
30 final object of the present invention is provide two-component polyurethane joint-sealing compositions which may be cured without the formation of bubbles when the substrate has a high moisture content, does not require solvents, results in products with exceptional mechanical properties after hardening and allows for a large variation in pot lives.

These objects may be achieved by the compositions according to the invention, described in more detail in the following, which contain alkylthio substituted aromatic diamines as a hardener or hardener component for organic polyisocyanates in two-component systems which react at room temperature to form polyureas.

SUMMARY OF THE INVENTION

The present invention relates to a coating composition or joint-sealing composition which may be cured at room temperature to form bubble-free products and contains

- i) a polyisocyanate component and
- ii) a hardener component containing
 - a) one or more aromatic diamines having at least one methyl substituent and at least one alkylthio substituent with 1 to 4 carbon atoms in the ortho position to each amino group and
 - b) optionally one or more organic polyhydroxyl compounds or organic polyamines other than those set forth in a).

DETAILED DESCRIPTION OF THE INVENTION

The properties of the diamines necessary for the invention and methods for their production are described in US Patents 4,670,598, 4,751,330, 4,866,209 and 4,889,955. Their synthesis is summarized in an article by P.F. Ranken and B.G. McKinnie in J. Org. Chem. 1989, 54 (12), 2985-2988. The articles by C.J. Nalepa and A.A. Eisenbraun in J. Elastomers Plast. 1987, 19 (1), 6-21, and by C.J. Nalepa et al. in J. Elastomers Plast. 1988, 20 (2), 128-142 in particular, provide a broad survey of the main applications of diprimary aromatic diamines. They mention in particular an application to prepare polyurethane elastomers with improved thermal stability and easier adaptation to various processing conditions due to a large variation in reactivity of the amine hardener as well as with clear improvements with regard to processability and mechanical properties. The possibilities for using the diamines mentioned

in this prior printed publication relate exclusively to their use in combination with NCO prepolymers in reaction mixtures to be cured to obtain elastomeric plastics at elevated temperatures. There is no reference at all in this prior printed publication to the use of the diamines in coating compositions or joint-sealing compositions which are to be cured at room temperature.

The two-component composition of the present invention contains a polyisocyanate component (i) and a hardener component (ii).

The type of polyisocyanate component (i) to be used is guided by the requirements which are placed on the coatings prepared from it:

- A) manually-processable two-component coating compositions having good resistance to weather and UV and relatively long pot lives or
- B) manually or mechanically processable two-component coating compositions having relatively short pot lives.

The polyisocyanate component (i) has an NCO content of 1 to 34% by weight. In addition to the type of NCO groups (which may be (cyclo)aliphatically or aromatically bound), the type of hardener component (ii) (which may be exclusively diamines or mixtures thereof with polyhydroxyl compounds) and the presence or absence of catalysts, the reactivity of the system also depends upon the NCO content of component (i).

To prepare systems of type A), aromatic polyisocyanates may be used (for example TDI prepolymers) if their NCO content is less than 8% by weight. However, it is preferred for the polyisocyanate component of type A) systems to exclusively contain (cyclo)aliphatically bound isocyanate groups. In particular, if polyisocyanate component (i) contains (cyclo)aliphatically bound isocyanate groups and is combined with hardeners (ii) which contain more than 20 equivalent percent of alcoholic hardener components, the NCO content of component (i) should be 10 to 25% by weight. If the hardener

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percent of alcoholic hardener components, the NCO content of component (i) should be 10 to 25% by weight. If the hardener component contains less than 20 equivalent percent of alcoholic hardener components, then polyisocyanate component (i) should
5 have an NCO content of 1 to 10% by weight when it contains (cyclo)aliphatic polyisocyanates (i) and is used to prepare type A) systems.

Polyisocyanates (i) which are used for the preparation of type A) systems are oligomeric polyisocyanates or NCO
10 prepolymers prepared from (cyclo)aliphatic diisocyanates, preferably hexamethylene diisocyanate (HDI) or 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) and optionally minor amounts of 4,4'-diisocyanato-dicyclohexylmethane. The oligomeric derivatives are known for use in
15 surface coating compositions, are prepared from monomeric diisocyanates and contain biuret, isocyanurate, urethane, allophanate and/or uretdione groups. The NCO prepolymers are prepared by reacting polyisocyanates with known organic
polyhydroxyl compounds, preferably organic polyether polyols or
20 polyester polyols.

These polyhydroxyl compounds which are used to prepare the prepolymers have a molecular weight (M_n , which may be calculated from the functionality and the hydroxyl group content) of 134 to 8,000, preferably 600 to 6,000, and a
25 hydroxyl functionality of 2 to 4, preferably 2 to 3.

The polyether polyols are prepared in known manner by the alkoxylation of suitable starting molecules (such as water, ethylene glycol, propanediol-1,2, trimethylolpropane, glycerine, pentaerythritol or mixtures thereof) with propylene
30 oxide and/or ethylene oxide, preferably exclusively propylene oxide. Preferred polyether polyols are polypropylene glycol and/or propoxylated trimethylolpropane.

Suitable polyester polyols for preparing the NCO prepolymers are prepared from polybasic, preferably dibasic, carboxylic acids (such as adipic acid, phthalic acid and hexahydrophthalic acid) and alcohols such as those described for preparing the polyether polyols. Also suitable are polycarbonate polyols, which may be obtained by reacting the previously described alcohols with diaryl carbonates in known manner, and the known polymerization products of γ -caprolactone which have hydroxyl groups.

As previously discussed, the type A) systems may also be based on NCO prepolymers prepared from aromatic polyisocyanates such as 2,4- and/or 2,6-diisocyanatotoluene, provided that the NCO content of the prepolymers falls within the above-mentioned limits.

To prepare the fast curing type B) systems, suitable polyisocyanates are preferably the polyisocyanate mixtures of the diphenylmethane series, which may be obtained by the known phosgenation of aniline/formaldehyde condensates and which preferably have a diisocyanatodiphenylmethane isomer content of 40 to 95% by weight and also contain higher homologs of these diisocyanates. Also suitable for preparing type B) systems are NCO prepolymers based on 2,4- and/or 2,6-diisocyanatotoluene, preferably having an NCO content of 1 to 14% by weight. Other suitable polyisocyanates having aromatically bound isocyanate groups are 1,5-diisocyanatonaphthalene and the polyisocyanate containing urethane groups which is obtained by reacting 1 mole of trimethylolpropane with 3 moles of 2,4-diisocyanatotoluene.

The diprimary aromatic diamines which are used in hardener component ii) have at least one alkylthio substituent with 1 to 4 carbon atoms in an ortho position to each amino group and at least one methyl substituent. The molecular weight of these diamines is between 168 and 298. Examples of these aromatic diamines include 1-methyl-3-methylthio-2,4-diaminobenzene, 1-methyl-3,5-bis(methylthio)-2,4-diaminobenzene, 1-methyl-3,5-bis(methylthio)-2,6-diaminobenzene, 1-methyl-3,5-

bis(ethylthio)-2,4-diaminobenzene, 1-methyl-3,5-bis(ethylthio)-2,6-diaminobenzene, 1-methyl-3,5-bis(butylthio)-2,4-diaminobenzene, 1-methyl-3,5-bis(butylthio)-2,6-diaminobenzene or mixtures of these
5 diamines. Preferred is a commercially available mixture of diamine isomers (available from Ethyl Corporation under the name Ethacure) containing 1-methyl-3,5-bis(methylthio)-2,4-diaminobenzene and 1-methyl-3,5-bis(methylthio)-2,6-diaminobenzene. To provide special properties (e.g., structural
10 viscosity), hardener (ii) in the two-component coating compositions produced by the process according to the invention may also contain small amounts of other diprimary, aromatic, sulphur-free, diamines, such as mixtures of 2,6-diethyl-1,3-diamino-4-methylbenzene and 4,6-diethyl-1,3-diamino-2-methyl-
15 benzene.

In addition, hardener component (ii) may contain in total up to 75 equivalent percent, based on the groups reactive with isocyanate groups, of organic polyhydroxyl compounds having an average hydroxyl functionality of 2 to 3. The use of these
20 polyhydroxyl compounds represent one of several possibilities for optimally adjusting the reactivity of the system and the properties of the cured end product to the particular requirements of each application.

The use of alcoholic hardener components is considered in particular in the preparation of type A) systems when using
25 polyisocyanates (i) having (cyclo)aliphatically bound isocyanate groups. If these polyisocyanate components have an NCO content of 10 to 25% by weight, component (ii) preferably contains up to 60 equivalent percent of polyhydroxyl compounds,
30 based on the total equivalents of isocyanate reactive groups present in component (ii). If the NCO content of component (i) is less than 10% by weight, then component (ii) preferably contains up to 20 equivalent percent of polyhydroxyl compounds, based on the total equivalents of isocyanate reactive groups present in component (ii).

Polyhydroxyl compounds which may be used as a portion of component (ii) are preferably the higher molecular weight polyhydroxyl compounds previously described as suitable for preparing the NCO prepolymers. In addition, polyether polyols modified with disperse polymer phases as described, for example, in DE-AS 1,260,142, 2,513,815, 2,723,293 or US-PS 4,716,210, or polybutadiene polyols may also be used to produce desired properties. Lower molecular weight polyols (such as ethylene glycol, propylene glycol, butanediol-1,4, hexanediol-1,6, glycerine and/or trimethylolpropane may also be used in small amounts in component (ii).

Components (i) and (ii) are preferably used for the preparation of coating compositions or joint-sealing compositions in amounts such that the equivalent ratio of isocyanate groups in component (i) to groups which are reactive with isocyanate groups in component (ii) is 0.8:1 to 2.5:1. Equivalent ratios of more than 1.2:1 are particularly suitable when oligomeric HDI and/or IPDI derivatives are used as component (i). When preparing type B) systems the equivalent ratio is preferably 0.9:1 to 1.3:1.

It is often desirable to add to either the type A) or B) systems, in addition to the binder components (i) and (ii), 0.1 to 5% by weight, preferably 0.5 to 2% by weight, of organic, preferably cycloaliphatic, carboxylic anhydrides (such as hexahydrophthalic anhydride or methylhexahydrophthalic anhydride) to greatly improve the cure rate.

The coating compositions to be used according to the invention may also contain the additives and auxiliaries known from coatings technology.

Although solvent-free coating compositions are preferred, they may contain up to 20, preferably up to 10 % by weight, based on the total weight of the coating composition, of the known lacquer solvents such as xylene, solvent naphtha, butyl acetate, 1-methoxypropyl-2-acetate or isoparaffins.

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Other auxiliaries and additives include pigments, fillers, UV-protectors, anti-oxidants, microbicides, fungicides, algacides, thixotropic agents, wetting agents, flow control agents, plasticizers, extenders (tar, tar substitutes, bitumen, etc.), other hardening catalysts and degassing agents.

5 The coating compositions to be used according to the invention generally possess (at 23° C) a pot life of about 20 minutes to 10 hours (type A) and about 20 seconds to 200 minutes (type B). The components (i) and (ii) possess each a viscosity at 23° C between 0.15 and 100 Pa.s (type A) or between 0.05 and 100 Pa.s (type B).

10 The coating compositions may be used to coat any substrate by known methods, mechanically or manually, depending upon the composition. The preferred fields of use for the coating compositions to be used according to the invention are the
15 coating of mineral building materials which are often damp (such as concrete structures, concrete slabs and brickwork), especially when the resistance to wear and tear and the resistance to chemicals of the surfaces of the building materials may be improved by the coating. Examples which may
20 be mentioned for type A are the renovation of balconies, patios and pergolas, and also the coating of plastic foam matting for various applications. Examples for type B include the sealing of surfaces in bridges, tunnels or multi-story parking garages, the internal coating of concrete or stoneware pipes, the
25 building up of worn layers on metallic or mineral substrates, and the highly wear-resistant surface sealing of loading ramps and chutes, bulk goods containers, etc.

30 The particular advantage of the systems according to the invention is that highly elastic, homogeneous and therefore bubble-free coatings with good mechanical properties are produced when coating damp mineral substrates or highly porous, flexible substrates, after appropriate pre-treatment. In type A further advantages are the economical use of the aromatic hardener and application-ready formulations with pot lives

which may be varied over a broad time-scale in a simple manner. In type B further advantages are the relatively short full curing times and the readily variable pot lives. The process according to the invention is particularly suitable for the application of thick coatings, i.e., those having a dry film thickness of 0.2 to 5 mm, onto the previously mentioned substrates. Application is by known methods, e.g., manually with a paint-brush, roller or spreader (type A and type B polyisocyanates based on TDI) or by using special two-component spraying or pouring equipment.

The joint-sealing compositions to be used according to the invention are composed in the same way as the coating compositions described above. Since joint-sealing compositions are generally applied by hand, however, those compositions which have a sufficiently long pot life are clearly preferable. In addition, joint-sealing compositions are differentiated in principle from the coating compositions containing the same binder systems mainly with regard to hardness: appropriate formulating generally sets the hardness of a sealing composition at Shore A 30 to Shore A 80, preferably Shore A 40 to Shore A 70.

In a particularly preferred embodiment of the present invention the joint-sealing compositions may be prepared by simply thoroughly shaking together readily miscible starting components (i) and (ii). In particular, polyisocyanate mixtures of the diphenylmethane series having an NCO content of 16 to 34%, preferably 29 to 33%, by weight are used as component (i), and diprimary aromatic diamines which may be mixed with up to 50 equivalent percent, preferably up to 40 equivalent percent, based on the total equivalents of component (ii), of polyether polyols are used as component (ii). These polyether polyols are preferably those having a hydroxyl group content of less than 2.0%, more preferably less than 1.5% by weight.

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It may also be expedient to add to the joint-sealing compositions the organic carboxylic anhydrides described for addition to the coating compositions in the amounts set forth.

5 The joint-sealing compositions to be used according to the invention may also contain the known auxiliaries and additives which are common in sealing compositions, such as solvents (in amounts of less than 20%, preferably less than 10%, by weight), plasticizers (monomeric or polymeric), pigments, fillers, UV-stabilizers, anti-oxidants, biocidal additives, wetting
10 agents, foam preventing agents or hardening catalysts.

In general, the components (i) and (ii) of the joint-sealing compositions possess each a viscosity of between 0.15 and 100 Pa.s at 23° C. The pot life of the joint-sealing compositions (at 23° C) is about 20 minutes to 10 hours. The sealing

15 compositions to be shaken should have a viscosity for each of the two components of less than 3.0, preferably less than 2.5 Pa.s at 23°C and a pot life (also at 23°C) of between 5 and 30 minutes.

20 The sealing compositions according to the invention may be used in known manner to plug floor joints between any substrates and gaps or pitting in flooring (defects), after appropriate substrate pretreatment. The preferred applications are where a certain resistance to various chemicals (mild acids or bases, mineral oil derivatives, "mild" solvents and chemical
25 intermediates) is required in addition to high permanent elasticity, without using heavy metal additives or chlorinated paraffins (prevention of water pollution). This situation arises in industrial flooring areas, tank farms, refineries, chemical plants, especially in concrete troughs or vats, and in
30 the floor-joints between concrete slabs or shaped blocks which make up a floor covering. The particular advantage of the joint-sealing compositions is their high permanent elasticity and resistance to chemicals, which is based on the fact that bubble-free full curing is facilitated even when the sides of the joint are wet in the floor area.

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The preferred applications for the shaken sealing compositions according to the invention are wherever horizontal (or approximately horizontal) expansion joints are to be sealed or damaged areas have to be repaired in the flooring of buildings, in the shortest time and using the simplest means, during the course of renovation or repair work. The application of the (self-levelling) sealing compositions according to the invention takes place in known manner.

The process according to the invention is explained further in the following examples wherein all parts and percentages are by weight unless otherwise indicated.

EXAMPLES

The following raw materials were used in the examples:

Isocyanate Components

Isocyanate Component A

A polyisocyanate mixture containing uretdione and isocyanurate groups, prepared from HDI, having an NCO content of 22%, containing less than 0.5% of free hexamethylene diisocyanate and having a viscosity of about 200 mPa.s (23°C).

Isocyanate Component B

A clear NCO prepolymer having an NCO content of 3.5% and a viscosity of 7 Pa.s at 23°C was obtained by reacting 750 parts of 2,4-diisocyanatotoluene at 100°C with 4000 parts of a polypropylene polyether polyol having a molecular weight of 3000, which was obtained by propoxylation of trimethylolpropane.

Isocyanate Component C

An NCO prepolymer was prepared by reacting 2000 parts of 2,4-diisocyanatotoluene and 500 parts of 2,6-diisocyanatotoluene at 100°C with 3150 parts of a polypropylene glycol having a molecular weight of 2000 and 850 parts of a polypropylene glycol having a molecular weight of 1000. Excess diisocyanatotoluene was removed from the prepolymer in a thin layer evaporator at a pressure of 0.1 mbar and at a temperature between 120 and 160°C. A clear liquid was obtained which had

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an NCO content of 4.4%, a residual content of unreacted diisocyanatotoluene of less than 05% and a viscosity of 6 Pa.s at 23°C.

Isocyanate Component D

5 An oligomeric MDI derivative prepared by the phosgenation of aniline/formaldehyde condensation products followed by partial removal by distillation of 4,4'-diisocyanatodiphenylmethane, containing 15% of higher functional homologs of MDI and 35 to 40% of 2,4'-diisocyanato-diphenylmethane and having
10 an NCO content of 32.5% and a viscosity of about 50 mPa.s (23°C).

Hardener A

An 80:20 mixture of the 2,4- and 2,6-isomers of 1-methyl-3,5-bis(methylthio)-diaminobenzene having a viscosity at 20°C
15 of about 700 mPa.s (available as Ethacure 300 from Ethyl Corporation).

Hardener B

A polyester diol prepared from hexanediol-1,6 and ε-hydroxycaproic acid, having a hydroxyl group content of about
20 1.6%, a viscosity at 75°C of about 1050 mPa.s and present as a yellowish liquid which is very viscous at room temperature.

Hardener C

A polyether polyol having a hydroxyl group content of 1.1% and a viscosity of 900 mPa.s at 23°C and prepared by the
25 propoxylation and subsequent ethoxylation of trimethylolpropane (PO:EO weight ratio - 86.5:13.5).

Hardener D

A graft polyether prepared according to DE-AS 2,513,815 and having a hydroxyl group content of 0.85% and a viscosity of
30 3300 mPa.s at 23°C.

Application and Comparison Examples

The following application or comparison examples were conducted with the previously described raw materials.

Application Example 1

This formulation can be used both as a thick coating composition and as a joint-sealing composition with sufficiently good resistance to UV.

5 The following constituents were homogeneously mixed in a vacuum dissolver and drawn off as components (i) and (ii):

370.5 parts of Isocyanate Component A as component (i);
49.5 parts of Hardener A, 448.5 parts of Hardener B, 3
10 parts of a 10% strength solution of dibutyltin dilaurate in solvent naphtha, 72 parts of an about 50% strength paste of a zeolite (pore diameter about 3 Å) in castor oil, 70 parts of Neuburger silica (an agglomerate of particulate quartz and laminar kaolinite; "Sillitin Z", Hoffmann and Söhne), 400 parts
15 of barytes and 78 parts of pigment as component (ii).

Amount of diprimary aromatic diamines	
in component (ii)*	52 equivalent %
(NCO:[OH + NH ₂]) equivalent ratio	2.20 : 1
20 Processing time at 23°C	50 minutes

25 * In this example and those following, this data refers to the amount of diamine necessary for the invention in component (ii), based on the total equivalents of compounds capable of reacting with NCO groups

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Properties of the cured coating (about 1 mm thick):

	Hardness	Shore D 40
	Tensile strength (DIN 53504)	121%
	Resistance to tearing (DIN 53504)	7.3 N/mm ²
5	Resistance to further tearing (DIN 53515)	15.5 N/mm

The mechanical properties of the bubble-free cured coating, which was resistant to UV and weathering, were very good.

10 Application Example 2 (manually processable coating)

The following constituents were homogeneously mixed in a vacuum dissolver and drawn off as components (i) and (ii):

15 1114.5 parts of Isocyanate Component C and 10.5 parts of methylhexahydrophthalic anhydride as component (i);

120 parts of Hardener A, 10.5 parts of degassing agent (Bevaloid 6420), 45 parts of pigment and 199.5 parts of barytes as component (ii).

20	Amount of diprimary aromatic diamines in B-component (ii)	100 equivalent %
	(NCO:NH ₂) equivalent ratio	1.04 : 1
	Processing time at 23°C	60 minutes

25 Properties of the cured coating (1.0 - 1.5 mm thick):

	Hardness	Shore A 89, D 35
	Tensile strength (DIN 53504)	530%
	Resistance to tearing (DIN 53504)	22 N/mm ²
30	Resistance to further tearing (DIN 53515)	60 N/mm

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The mechanical properties of the bubble-free, cured, thick test films were excellent.

Application Example 3 (manually processable coating)

5 This variant of Example 2 verifies the ready adaptability of the curing technique by simply varying the basic formulation.

With the exception of the proportion of methylhexahydrophthalic anhydride, which was omitted, the formulation was the same as in application Example 2.

10 While the mechanical properties of the test films remained essentially unchanged, the processing time at 23°C was extended to 90 minutes.

Application Example 4 (manually processable coating)

15 The following constituents were homogeneously mixed in a vacuum dissolver and drawn off as components (i) and (ii):

1114.5 parts of Isocyanate Component B and 10.5 parts of methylhexahydrophthalic anhydride as component (i);

20 105 parts of Hardener A, 10.5 parts of degassing agent (Bevaloid 6420), 45 parts of pigment and 214.5 parts of barytes as component (ii).

Amount of diprimary aromatic diamine	100 equivalent %
in component (ii)	
(NCO:NH ₂) equivalent ratio	0.95 : 1
25 Processing time at 23°C	60 minutes

Properties of the cured coating (1.0 - 1.5 mm thick):

30 Hardness	Shore A 83, D 30
Tensile strength (DIN 53504)	420%
Resistance to tearing (DIN 53504)	7.4 N/mm ²
Resistance to further tearing (DIN 53515)	19.0 N/mm

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Application Example 5 (manually processable coating)

With the exception of the proportion of methylhexahydrophthalic anhydride, which was omitted, the formulation was the same as in application Example 4.

5 While the mechanical properties of the test films were essentially unchanged, the processing time at 23°C was extended to 90 minutes.

Application Example 6 (manually processable coating)

10 The following constituents were homogeneously mixed in a vacuum dissolver and drawn off as components (i) and (ii):

1117.5 parts of Isocyanate Component C and 7.5 parts of methylhexahydrophthalic anhydride as component (i);

15 90 parts of Hardener A, 30 parts of a phenylalkyl sulphate plasticizer (Mesamoll, Bayer AG), 10.5 parts of a degassing agent (Bevaloid 6420), 45 parts of pigment, 3 parts of a pyrogenic silica with a small water content (Cab-O-sil TS 720, Cabot) and 196.5 parts of barytes as component (ii).

20	Amount of diprimary aromatic diamine	
	in component (ii)	100 equivalent %
	(NCO:NH ₂) equivalent ratio	1.4 : 1
	Processing time at 23°C	90 minutes

Properties of the cured coating (1.0 - 1.5 mm thick):

25	Hardness	Shore A 80
	Tensile strength (DIN 53504)	540%
	Resistance to tearing (DIN 53504)	18.0 N/mm ²
	Resistance to further tearing (DIN 53515)	40.0 N/mm

30 The mechanical properties of the bubble-free, cured, thick test films were excellent.

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Application Example 7 (manually processable coating)

The following constituents were homogeneously mixed in a vacuum dissolver and drawn off as components (i) and (ii):

1117.5 parts of Isocyanate Component C and 7.5 parts of methylhexahydrophthalic anhydride as component (i);

60 parts of Hardener A, 60 parts of a phenylalkyl sulphonate plasticizer (Mesamoll, Bayer AG), 10.5 parts of a degassing agent (Bevaloid 6420), 45 parts of pigment, 3 parts of a pyrogenic silica with a small water content (Cab-O-sil TS 720, Cabot) and 19.5 parts of barytes as component (ii).

Amount of diprimary aromatic diamines	
in component (ii)	100 equivalent %
(NCO:NH ₂) ratio of equivalents	2.1 : 1
Processing time at 23°C	150 minutes

Properties of the cured coating (1.0 - 1.5 mm thick):

Hardness	Shore A 60
Tensile strength (DIN 53504)	650%
Resistance to tearing (DIN 53504)	17.0 N/mm ²
Resistance to further tearing (DIN 53515)	34.0 N/mm

The mechanical properties of the bubble-free, cured, thick test films were excellent.

Comparison Example 1 (Use of a diamine not according to the invention)

Application Example 2 was repeated with the exception that instead of the 120 parts of Hardener A, component (ii) contained 146 parts of a 67% strength solution of a 2:1 mixture of the 2,4- and 2,6-isomers of 1-methyl-3,5-diethyl-diaminobenzene in propylene carbonate (4-methyl-1,3-dioxolan-2-one). The (NCO:NH₂) equivalent ratio was identical with that of application Example 2.

A processing time of only about 400 seconds was found.
Application Example 8 (coating to be processed mechanically)

The following constituents were homogeneously mixed in a vacuum dissolver and drawn off as components (i) and (ii):

5 289.5 parts of Isocyanate Component D and 210 parts of Hardener B for component (i), (the NCO content drops from 18.8 to 17.2% by preliminary reaction in the drums);

10 827 parts of Hardener B, 114 parts of hardener A, 57 parts of an about 50% strength zeolite paste (pore diameter about 3 Å) in castor oil and 4.5 parts of dibutyltin dilaurate for component (ii).

Amount of diprimary aromatic diamine	
in B-component (ii)	58 equivalent %
(NCO:[OH+NH ₂]) ratio by equivalents	1.11 : 1

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20 Using a two-component airless spray unit, the material was preheated to 70°C and sprayed out to a thickness of about 1.5 mm. The pot life was less than 1 minute. The resulting sprayed coating which lost its surface stickiness (tackiness) after about 30 minutes, has the following mechanical properties:

Hardness	Shore A 80, D 30
Tensile strength (DIN 53504)	300%
Resistance to tearing (DIN 53504)	20.0 N/mm ²
Resistance to further tearing (DIN 53515)	31.0 N/mm

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30 These figures for the mechanical properties were very high for sprayed, thick, elastic sealants. Another test sample was obtained by mechanical two-component casting. Performance of a test to determine the resistance to abrasive wear and tear according to DIN 53516 produced an extraordinarily high result of 35 mm³.

Application Example 9 (coating to be processed mechanically)

20,000 parts of an MDI prepolymer having an NCO content of 8.6% and a viscosity of 3.1 Pa.s at 23°C and prepared by reacting a mixture containing 65% of 2,4'- and 35% of 4,4'- diisocyanatodiphenylmethane with a polypropylene glycol having a molecular weight of 4,000 as component (i) and 3600 parts of Hardener A as component (ii) were heated to 50°C and, using a two-component mixing unit, poured out to give a film having a thickness of about 2 mm.

Amount of diprimary aromatic diamines
in component (ii)
(NCO:NH₂) ratio of equivalents
Pot life

100 equivalent %
1.22 : 1
1 minute

Properties of the cured thick coating:

Hardness	Shore A 95, D 45
Tensile strength (DIN 53504)	95%
Resistance to tearing (DIN 53504)	8.0 N/mm ²
Resistance to further tearing (DIN 53515)	62.0 N/mm

The mechanical properties were very good indeed for a mechanically applied surface seal.

Application Example 10 (shaken sealing composition)

Component (i) was produced in a dissolver by mixing 680 parts of Isocyanate Component D and 20 parts of a paste containing pigments and butylbenzyl phthalate as plasticizer, component (ii) was also made in a dissolver by mixing 1400 parts of Hardener C, 1360 parts of Hardener D, 300 parts of Hardener A, 140 parts of an about 50% strength zeolite paste (pore diameter about 3Å) in castor oil, 120 parts of a paste containing pigments and butylbenzyl phthalate as plasticizer, 20 parts of degassing agent (Bevaloid 6420), 60 parts of a 10% strength solution of dibutyltin dilaurate in an aromatic

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hydrocarbon and 1000 parts of a phosphate-ester plasticizer (Disflamoll TOF; Bayer AG).

Characteristic properties of the shaken sealing composition:

	Amount of diprimary aromatic diamine	
5	in component (ii)	64 equivalent %
	(NCO:[OH+NH ₂]) ratio of equivalents	1.2 : 1
	Processing time at 23°C	15 minutes
	Pot life at 23°C	20 minutes
	Viscosity of component (i) at 23°C	about 50 mPa.s
10	Viscosity of component (ii) at 23°C	about 2000 mPa.s

Properties of the cured shaken sealing composition:

	Hardness	Shore A 67
15	Tensile strength (DIN 53504)	220%
	Resistance to tearing (DIN 53504)	6.5 N/mm ²
	Resistance to further tearing (DIN 53515)	7.5 N/mm

20 This example demonstrates the outstanding suitability of the sealing compositions according to the invention.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention
25 except as it may be limited by the claims.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A coating composition or joint-sealing composition which may be cured at room temperature to form bubble-free products comprising

- i) a polyisocyanate component and
- ii) a hardener component comprising
 - a) one or more aromatic diamines having at least one methyl substituent and at least one alkylthio substituent with 1 to 4 carbon atoms in the ortho position to each amino group and
 - b) optionally one or more organic polyhydroxyl compounds or organic polyamines other than those set forth in a).

2. The composition of Claim 1 wherein the component a) is present in an amount of at least 20 equivalent percent, based on the total number of isocyanate reactive groups present in component ii) and the equivalent ratio of isocyanate groups in component i) to isocyanate reactive groups in component ii) is 0.8:1 to 2.5:1.

3. The composition of Claim 1 wherein the polyisocyanate component has an NCO content of 1 to 34% by weight and comprises at least one organic polyisocyanate selected from the group consisting of (i) di- and/or polyisocyanates of the diphenylmethane series, (ii) NCO prepolymers prepared from 2,4- and/or 2,6-diisocyanatotoluene and (iii) oligomeric polyisocyanates having biuret, isocyanurate, urethane, allophanate and/or uretdione groups and prepared from hexamethylene diisocyanate and/or 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane.

4. The composition of Claim 2 wherein the polyisocyanate component has an NCO content of 1 to 34% by weight and comprises at least one organic polyisocyanate selected from the group consisting of (i) di- and/or polyisocyanates of the diphenylmethane series, (ii) NCO prepolymers prepared from 2,4- and/or 2,6-diisocyanatotoluene and (iii) oligomeric

polyisocyanates having biuret, isocyanurate, urethane, allophanate and/or uretdione groups and prepared from hexamethylene diisocyanate and/or 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane.

5 5. The composition of Claim 1 wherein said diprimary aromatic diamine comprises 1-methyl-3,5-bis(methylthio)-2,4-diaminobenzene and/or 1-methyl-3,5-bis(methylthio)-2,6-diaminobenzene.

10 6. The composition of Claim 2 wherein said diprimary aromatic diamine comprises 1-methyl-3,5-bis(methylthio)-2,4-diaminobenzene and/or 1-methyl-3,5-bis(methylthio)-2,6-diaminobenzene.

15 7. The composition of Claim 3 wherein said diprimary aromatic diamine comprises 1-methyl-3,5-bis(methylthio)-2,4-diaminobenzene and/or 1-methyl-3,5-bis(methylthio)-2,6-diaminobenzene.

20 8. The composition of Claim 4 wherein said diprimary aromatic diamine comprises 1-methyl-3,5-bis(methylthio)-2,4-diaminobenzene and/or 1-methyl-3,5-bis(methylthio)-2,6-diaminobenzene.

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